EFFECT OF EFFLUENT COMPOSITION VARIABLES ON FLOCCULATION OF SUSPENDED SOLIDS IN LIME-SULFIDE UNHAIRING EFFLUENTS*

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ABSTRACT

Previous research at ERRC has shown that high sulfide hair-burn unhairing effluents which differ widely in composition require different chemical flocculants for optimum reduction of suspended solids. We have now determined the ranges of composition variables (pH, salt content, suspended solids and soluble organic material) in which specific flocculation treatments remain effective for paddle vat and low float hide processor effluents by deliberate adjustment of standard commercial unhairing effluents. While the sensitivity to changes in composition varied with type of effluent and chemical flocculant being used, the effectiveness of treatments generally varied only slightly over the range of zero to five percent sodium chloride concentration. Compositional changes taking place in the highly alkaline effluents during holding periods of less than one week had little effect on treatment effectiveness.

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INTRODUCTION

The removal of hair from cattlehides by the hair pulping process produces effluents with high concentrations of suspended solids. The suspended solids can represent 30–50 percent of total solids in the effluents. We have been working on methods for reduction of the suspended solids from lime-sulfide effluents by flocculation, without altering the pH of the effluents. Cooper *et al.* (1) developed procedures for coagulating and flocculating the suspended solids from fresh hide, paddle vat unhairing effluents which involved addition of an anionic polyelectrolyte, followed by a cationic polyelectrolyte, and then by sodium hexametaphos-

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†Retired.

TABLE I

EXPERIMENTAL FLOCCULATING AGENTS

Flocculant	Type
Percol 720	Nonionic
" 721	Low cationic
" 722	Medium cationic
" 725	High anionic
" 726	Medium anionic
" 730	Low anionic
" 763	High cationic
Mineral Colloid 101	Inorganic
" " 103	Inorganic
SGP-100	Nonionic
X-400	Anionic
PFA-10	Anionic
PFC-3	Cationic
$(NaPO_3)_6$	Inorganic

One percent solutions or suspensions of each solid flocculant were prepared by dispersing one gram of the solids into the vortex of 100 ml. of water stirred magnetically and heated to 65–75°C. The liquid flocculants were diluted to one percent solutions with water. Aliquots of these stock solutions were used in the flocculation tests.

Flocculation Procedure

The flocculation procedure reported previously by Cooper *et al.* (1) and Bitcover *et al.* (2) was used. One liter samples of screened effluent were transferred to six 1500 ml. beakers and stirred at 100 r.p.m., with a Phipps & Bird apparatus, while the flocculating agents were added. Aliquots of the one percent stock solutions of polyelectrolytes were pipetted into the beakers to provide a range of concentrations from 0 to 100 mg./l. The stirring rate was maintained for five min. at 100 r.p.m., then decreased to 25 r.p.m. for an additional 20 min. to promote flocculation. When more than one flocculant was added, the effluent was stirred for five min. at 100 r.p.m. after each addition, prior to final stirring at 25 r.p.m. The floc was allowed to settle for 30 min., then 10 ml. of the supernatant liquor was pipetted from 2.5 cm. below the surface for determination of suspended solids and other components. Controls without the added polyelectrolytes were run with each experiment.

Composition Variables

The effects of screening and flocculation on the various fractions of hide processor and paddle vat effluents were studied. These fractions were unscreened effluent, screened effluent, solids settled for 30 min., and supernatant liquor. The following composition variables in each fraction were determined: total solids, volatile solids, suspended solids, chemical oxygen demand (COD), total alkalinity, pH, sodium sulfide, total ash, calcium oxide, total fat, total nitrogen, and organic nitrogen.

Effluent Parameters

We studied the effects of the following parameters on the efficiency of polyelectrolyte flocculants for the removal of suspended solids from lime-sulfide unhairing effluents: age of the effluent, suspended solids content, salt content, dilution of the effluent, pH of the effluent, air-oxidation with $MnSO_4$ as a catalyst, and screening.

Effluent Age. Screened paddle vat effluent was treated with the Primafloc flocculant system†† developed by Cooper *et al.* (1) (PFA-10, 30 mg./l.; PFC-3, 0.3 mg./l.; $(NaPO_3)_6$, 30 mg./l.; added in that order) at the initial period and after holding periods of one, two, and three weeks at room temperature. The effects of aging (holding period) on flocculation were determined by measuring the concentrations of the suspended solids.

Salt Content. Portions of screened paddle vat unhairing effluent were made to contain two percent, five percent, and eight percent NaCl, based on the volumes of effluent. The test samples then were flocculated with the Primafloc flocculant system, and the effects of the added NaCl were determined by measuring the concentrations of the suspended solids.

Combined Aging and Salt Content. The combined effects of aging and salt content were studied by making up portions of screened paddle vat effluent to contain two percent, five percent, and eight percent NaCl, and flocculating them with the Primafloc flocculant system after aging them for zero, one, two, and three weeks at room temperature. The results were determined by measuring the concentrations of the suspended solids.

Effluent Dilution. Water was added to portions of screened hide processor and paddle vat effluents in amounts from one-half to three times the volume of the original effluents. The hide processor samples were flocculated with 25 mg./l. of X-400, and the paddle vat samples were flocculated with the Primafloc flocculant system. The results were determined by measuring the suspended solids.

Effluent pH. The effects of pH changes on the unhairing effluents were determined in two types of studies. In the first study, portions of screened paddle vat effluent and screened hide processor effluent were adjusted to pH's 12, 11, and 10 with 1:1 HCl. The paddle vat samples were then flocculated with the Primafloc flocculant system, and the hide processor samples were flocculated with 25 mg./l. of X-400. The effects of pH were determined by measuring the concentrations of the suspended solids.

††Hereafter so identified.

In the second study, portions of screened paddle vat effluent were adjusted to a series of pH's from 12 to 4.5 with 1:1 HCl or with SO_2 gas which was bubbled slowly into each sample. The effects of altering the pH were determined by measuring the changes in the suspended solids.

Flocculation of Air-Oxidized Hide Processor Effluent. Portions of screened hide processor effluent, which had been treated with air and $MnSO_4$ catalyst to oxidize the sulfides, were treated with the most effective concentrations for promoting flocculation (as determined in the earlier tests (2)) of SGP-100, X-400, the Primafloc flocculant system, and Percols 720, 721, 726, 730, and 763. The effects of these polyelectrolytes on flocculation were determined by measuring the concentrations of the suspended solids.

Screening. The effects of screening were studied with standard sieves, mesh numbers 10, 20, 30, 40, and 50. Portions of unscreened paddle vat effluent were poured through the 20 cm. diameter screens, and one liter portions were collected in 1500 ml. beakers. The solids retained on the screens were carefully transferred to porcelain evaporating dishes and dried on a steam bath, and finally in a 105°C. drying oven. Determinations of total solids, suspended solids, volatile suspended solids, total nitrogen, total alkalinity, total fat, and COD were made on the screened effluents.

Analytical Methods

The official methods of analysis of the American Public Health Association, American Water Works Association, and Water Pollution Control Federation were used for the determinations of pH, COD, total solids, total volatile solids, suspended solids, volatile suspended solids, and total alkalinity (3). Total and organic nitrogen were determined by the semi-micro Kjeldahl method (4). Sodium sulfide was determined by the Official Method of Analysis of the Society of Leather Trades Chemists (5). Calcium oxide was determined with a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer equipped with a triple-slot burner (6, 7).

RESULTS AND DISCUSSION

Previous results have shown that different flocculant systems are required for efficient removal of the suspended solids from different unhairing effluents. The effects of screening, settling, and flocculation on the compositions of hide processor and paddle vat unhairing effluents are summarized in Tables II and III, respectively. The COD, total solids, suspended solids, and total alkalinity were reduced in successive amounts by screening, settling, and flocculation. The large amounts of lime (CaO) in the settled, flocculated solids (approximately 65 percent and 76 percent) compared with the settled, unflocculated solids (21 percent and 28 percent) of the hide processor and paddle vat unhairing effluents, respectively, agree with previous findings (2). The settled solids contain nearly

TABLE II

EFFECT OF SCREENING, SETTLING, AND FLOCCULATION ON THE COMPOSITION OF HIDE PROCESSOR EFFLUENT

		Original Effluent				Flocculated Effluent (X-400)	
		* Unscreened	† Screened	‡ Supernatant Liquor	** MFB Settled Solids	†† Supernatant Liquor	‡‡ MFB Settled Solids
mg./l.	Chemical Oxygen Demand	119,128	112,210	70,526		58,536	
"	Total Solids	206,000	188,000	180,100		161,700	
"	Total Volatile Solids	74,000	54,000	64,940		57,710	
"	Initial Suspended Solids	82,540	64,500	35,115		35,115	
"	30′ Suspended Solids	—	—	23,430		3,275	
"	30′ Volatile Suspended Solids	44,520	26,313	12,700		1,150	
"	% Reduction, S. S.	—	34	34		91	
"	Total Alkalinity	46,460	37,733	16,400		11,900	
	pH	12.8	12.8	12.7		12.3	
	Total Ash, %	58.5	54	—	57	—	60
	Calcium Oxide, %	—	1.86	2.01	20.9	0.98	64.9
	Sodium Sulfide, %	0.72	0.76	0.81	—	0.90	—
	Total Fat, %	0.59	0.59	0.51	0.70	0.16	0.85
	Total Nitrogen, %	0.48	0.45	0.46	1.86	0.50	1.74
	Organic Nitrogen, %	0.45	0.43	0.45	1.84	0.48	1.70

*Analyses of unscreened effluents from the unhairing operation.
†Analyses of effluent screened through 50 X 50 mesh polypropylene screen.
‡Analyses of supernatant liquor above solids settled by gravity.
**Analyses of solids settled by gravity.
††Analyses of supernatant liquor above flocculated solids settled by gravity.
‡‡Analyses of flocculated solids settled by gravity.

TABLE III

EFFECT OF SCREENING, SETTLING, AND FLOCCULATION ON THE COMPOSITION OF PADDLE VAT EFFLUENT

		Original Effluent				Flocculated Effluent (PFA-10, PFC-3, $(NaPO_3)_6$)	
		* Unscreened	† Screened	‡ Supernatant Liquor	** MFB Settled Solids	†† Supernatant Liquor	‡‡ MFB Settled Solids
mg./l.	Chemical Oxygen Demand	64,961	53,731	48,711		50,148	
"	Total Solids	44,000	42,000	40,280		37,810	
"	Total Volatile Solids	30,000	24,000	26,180		27,130	
"	Initial Suspended Solids	25,160	12,387	12,175		12,175	
"	30′ Suspended Solids	—	—	2,315		2,870	
"	30′ Volatile Suspended Solids	19,160	6,947	9,450		1,760	
"	% Reduction, S. S.	—	24	24		77	
"	Total Alkalinity	13,910	13,150	13,100		9,685	
	pH	12.7	12.8	12.7		12.5	
	Total Ash, %	56	56	—	49	—	51
	Calcium Oxide, %	—	1.64	1.05	27.8	1.05	76.2
	Sodium Sulfide, %	0.49	0.45	0.45	—	0.40	—
	Total Fat, %	0.25	0.29	0.24	0.44	0.28	0.40
	Total Nitrogen, %	0.42	0.41	0.39	1.96	0.38	1.73
	Organic Nitrogen, %	0.39	0.37	0.37	1.93	0.35	1.68

*Analyses of unscreened effluents from the unhairing operation.
†Analyses of effluent screened through 50 X 50 mesh polypropylene screen.
‡Analyses of supernatant liquor above solids settled by gravity.
**Analyses of solids settled by gravity.
††Analyses of supernatant liquor above flocculated solids settled by gravity.
‡‡Analyses of flocculated solids settled by gravity.

two percent nitrogen. Both the CaO and N contents suggest the potential values of these materials as possible ingredients of fertilizer and/or feed mixes. After flocculation, the effluents contain high levels of soluble nitrogen-containing compounds, high sulfide-ion levels, and fats, so that secondary treatments will be required before discharge to the environment. Cooper *et al.* (8) reported some results of the effectiveness of biological oxidation treatments for the elimination of certain of these constituents.

Inspection of the effluent compositions listed in Table IV shows some differences which could possibly be responsible for the differences in flocculant behavior. The paddle vat effluent had less than 0.3 percent NaCl, while the hide processor effluent had about eight percent NaCl, which represents the salt carried over from the hide soaking operation. The suspended solids load of the paddle vat effluent was about one-fifth that of hide processor effluent. The volatile suspended solids content of the paddle vat effluent was about a fourth that of the hide processor effluent. The air-oxidized hide processor effluent had approximately the same concentrations of suspended solids and volatile suspended solids as the paddle vat effluent since it was diluted with soak and wash waters. Therefore, two obvious variables for study were dilution of the effluents and the concentrations of salt.

TABLE IV

PARTIAL COMPOSITION OF SCREENED UNHAIRING EFFLUENTS

	Paddle Vat Effluent	Hide Processor Effluent	
		Original	Oxidized
pH	12.8	13.0	12.9
NaCl, %	<0.3	8.0	2.7
Na_2S, %	0.45	0.72	0.005
Suspended Solids, mg./l.	12,400	64,500	13,700
Volatile Suspended Solids, mg./l.	7,800	26,300	7,000

Effluent Dilution. The effects on flocculation of adding from one half to three volumes of water to each volume of unhairing effluent are summarized in Table V. The dilutions resulted in marked reduction of suspended solids in both unflocculated effluents: amounts settled by gravity increased from 23 percent in undiluted paddle vat effluent to 51–69 percent in the diluted effluent, and from 45 percent to 91 percent in hide processor effluent. Flocculation reduced suspended solids in all dilutions, from 83–95 percent in the paddle vat effluent, and 91–96 percent in the hide processor effluent.

Usually hides are washed after unhairing, and the wash waters are combined with the unhairing waste liquors. The result may be a two to fourfold dilution

TABLE V

EFFECT OF DILUTION ON FLOCCULATION OF UNHAIRING EFFLUENTS

Dilution Effluent/H_2O	Paddle Vat Effluent*				
	Fresh, Screened			Flocculated	
	Suspended Solids			Suspended Solids	
	Before Settling	After Settling 30 min.	% Reduction	After Settling 30 min.	% Reduction
	(mg./l.)			(mg./l.)	
1:0	9,850	7,615	22.7	1,630	83.2
1:1/2	6,600	3,250	50.8	360	94.5
1:1	4,925	1,885	61.7	280	94.3
1:2	3,250	1,090	66.5	305	90.6
1:3	2,462	765	68.9	400	83.8
	Hide Processor Effluent†				
1:0	56,285	30,610	45.6	2,190	96.1
1:1/2	37,710	16,490	56.3	2,640	93.0
1:1	28,142	2,465	91.2	1,015	96.3
1:2	18,574	1,645	91.1	1,105	94.1
1:3	14,071	1,380	90.2	1,235	91.2

*Primafloc flocculant system.
†X-400, 25 mg./l.

TABLE VI

EFFECT OF SALT ON FLOCCULATION OF UNHAIRING EFFLUENT

Polyelectrolyte Conc. mg./l.	Paddle Vat Effluent			
	% Reduction, Suspended Solids			
	0% NaCl	2% NaCl	5% NaCl	8% NaCl
X-400				
3	48.9	—	—	51.6
6	48.0	—	—	50.4
9	45.5	—	—	49.3
50	38.6	31.3	31.0	38.0
SGP-100				
3	48.7	—	—	53.6
6	47.9	—	—	52.9
9	50.9	—	—	49.0
50	38.4	36.9	32.4	38.5
Primafloc Flocculant System	91.2	83.8	89.8	80.2

of the original unhairing liquor. These studies showed that the removal of suspended solids by specific flocculants was not affected by up to fourfold dilutions of the effluents with water.

Salt Concentration. The effects of NaCl concentration in the effluents upon flocculation are summarized in Table VI. Examination of Table IV shows that the NaCl content of the hide processor effluent used in these studies was about eight percent. When increments of NaCl up to eight percent were added to paddle vat effluent neither SGP-100 nor X-400 produced more than about 50 percent reduction in suspended solids. In hide processor effluent both of these polyelectrolytes reduced the suspended solids by over 90 percent. However, the Primafloc flocculant system reduced the suspended solids of paddle vat effluent by 80 to 90 percent at NaCl concentrations up to eight percent. The NaCl content of an unhairing effluent under normal conditions is evidently not a primary factor in the flocculating efficiency of polyelectrolytes.

Aging and NaCl Content. The combined effects of holding period and salt content do exert pronounced effects on the efficiency of flocculating agents. Some of these are summarized in Table VII. The control, with no NaCl added, showed

TABLE VII

EFFECTS OF AGING AND SALT CONCENTRATION ON FLOCCULATION OF UNHAIRING EFFLUENT

	(% Reduction, Suspended Solids) Paddle Vat Effluent*				
Weeks	Control†	0% NaCl	2% NaCl	5% NaCl	8% NaCl
0	26.8	91.2	83.8	89.8	80.2
1	28.3	91.8	83.1	78.0	67.6
2	28.5	81.8	78.0	78.0	60.0
3	20.7	84.8	70.3	66.6	—

*Primafloc flocculant system.
†No flocculants added.

an initial reduction of suspended solids, due to gravity settling, of 27 percent, no decrease after one and two weeks, and only a slight to moderate decrease after three weeks. Upon flocculation with the Primafloc flocculant system, the control showed an initial reduction of suspended solids of 91 percent, and only a moderate decrease after two and three weeks.

Aging combined with salt produced a considerable loss in flocculant efficiency. The addition of salt to produce five percent and eight percent concentrations in paddle vat effluent aged one week, resulted in a lower reduction of suspended solids by 13 percent and 23 percent, respectively. With two weeks aging, a significantly lower efficiency of flocculation was noted with increasing salt concentration, even at the level of two percent NaCl. Similar losses in flocculant efficiency were noted after three weeks of aging. The combined effects of increased salt content and aging of the effluents were both detrimental to flocculation of the suspended solids.

Effluent pH. Although flocculants are normally added directly to the unhairing effluents without any pH alterations of the effluents, a possibility exists that some pH changes of an effluent may inadvertently occur. The effects on flocculation of lowering the pH of screened paddle vat and hide processor effluents are summarized in Table VIII. Lowering the pH to 10 and 11 decreased

TABLE VIII

EFFECT OF pH ON FLOCCULATION OF UNHAIRING EFFLUENTS

pH*	Paddle Vat Effluent†		Hide Processor Effluent‡	
	Suspended Solids	% Reduction	Suspended Solids	% Reduction
	(mg./l.)		(mg./l.)	
Original** (12.5)	15,280		38,450	
12	1,340	91.2	2,680	93.0
11	6,660	56.4	14,680	61.8
10	6,170	59.6	12,420	67.7

*Adjusted with 1:1 HCl.
†Primafloc flocculant system.
‡X-400 (25 mg./l.).
**Before settling 30 min.

the effectiveness of the flocculants greatly. The removal of suspended solids was decreased from 91 percent to 56–59 percent in the case of paddle vat effluent, and from 93 percent to 62–68 percent in the case of hide processor effluent.

The effects on the levels of suspended solids of lowering the pH of an unhairing effluent to pH values as low as 4.5 are summarized in Table IX. Below about pH 8 proteins began to precipitate and this caused the level of suspended solids to decrease markedly. At pH 4.5, the isoelectric point of these proteins, the supernatant liquors were clear, and the settled solids were granular. HCl caused liberation of considerable quantities of H_2S as the pH was lowered, and SO_2 also liberated some H_2S from solution. The primary advantages of the original high pH of the effluents are the avoidance of liberation of noxious and highly toxic H_2S gas, and providing conditions for high flocculant efficiency.

New Polyelectrolytes

The results of the different polyelectrolytes that were tested in this study are summarized in Table X. None of the Percol 700 series polyelectrolytes showed

TABLE IX

EFFECT OF pH ON SUSPENDED SOLIDS OF UNHAIRING EFFLUENT

pH	Paddle Vat Effluent			
	Hydrochloric Acid		Sulfur Dioxide	
	Suspended Solids	% Reduction	Suspended Solids	% Reduction
	(mg./l.)		(mg./l.)	
Original* (12.5)	11,380		12,200	
12	8,490	25.4	8,485	30.5
10	5,470	52.0	6,305	48.4
9	5,270	53.7	5,570	54.3
8	5,140	54.8	3,075	74.8
7	3,100	72.8	2,880	76.4
6	1,740	84.7	2,255	81.5
4.5†	1,260	88.9	1,490	87.3

*Before settling 30 min.
†Isoelectric point of hair protein.

TABLE X

EFFECT OF VARIOUS POLYELECTROLYTES ON FLOCCULATION OF SCREENED UNHAIRING EFFLUENTS

Polyelectrolyte	Most Effective Concentration	% Reduction, Suspended Solids
	(mg./l.)	
Paddle Vat Effluent		
Percol 720	15	65.6
Percol 721	5	50.6
Percol 722	20	37.5
Percol 725	40	38.9
Percol 726	20	44.0
Percol 730	40	61.8
Percol 763	20	51.1
Mineral Colloid 101	100	50.7
Mineral Colloid 103	100	38.3
(Mineral Colloid 101	500	70.5
plus Alum.)	200	
(Mineral Colloid 101	500	89.1
plus $FeCl_3$)	400	
Primafloc Flocculant System		91.2
Control*		24.0
Hide Processor Effluent		
Percol 720	20	88.3
Percol 730	20	90.6
X-400	25	96.1
Control*		34.0

*With no polyelectrolyte.

any special merits for flocculatitng paddle vat effluent, although Percol and Percol 730 were satisfactory for flocculatitng hide processor effluent. The Mineral Colloids (Bentonite clays) were not sufficiently effective for flocculating paddle vat effluent, unless they were used in conjunction with alum or $FeCl_3$. In the case of $FeCl_3$, however, a black suspension of FeS results, which may be undesirable. For all these reasons, none of the newer polyelectrolytes had any particular merits which would recommend them in place of the Primafloc flocculant system or X-400, or SGP-100.

Effect of Polyelectrolytes on Flocculation of $MnSO_4$Catalyzed Air-Oxidized Hide Processor Effluent.

Hide Processor Effluent. Some tanners have adopted procedures for oxidizing the sulfides in unhairing effluents by air in the presence of $MnSO_4$ catalyst. The efficiency of removal of the suspended solids by flocculating agents might be affected by such treatment. Therefore, a series of flocculating agents, listed in Table XI were tried, and their results are summarized.

TABLE XI

EFFECT OF POLYELECTROLYTES ON FLOCCULATION OF $MnSO_4$-CATALYZED AIR-OXIDIZED HIDE PROCESSOR EFFLUENT

Polyelectrolyte	Most Effective Concentration	% Reduction, Suspended Solids
	(mg./l.)	
SGP-100	50	27.1
X-400	30	26.6
Percol 720	20	12.9
Percol 721	10	16.0
Percol 726	20	8.3
Percol 730	40	17.5
Percol 763	20	17.7
Primafloc Flocculant System		92.0

Since both X-400 and SGP-100 were effective in flocculating unoxidized hide processor effluent, these polyelectrolytes were tried first to flocculate the air-oxidized effluent. Neither of these flocculating agnts was useful in flocculating the air-oxidized effluent. When the flocculants of the Percol series were tried, none was effective either.

Considering the similarity in the concentrations of suspended solids of air-oxidized hide processor effluent and paddle vat effluent (Table IV) we tried the Primafloc flocculant system, which is effective in flocculating paddle vat effluent. The Primafloc flocculant system was effective in reducing the suspended solids of air-oxidized hide processor effluent about 92 percent.

The efficacy of air-oxidation for the removal of sulfides, in the presence of

TABLE XII

EFFECT OF SCREENING ON COMPOSITION OF PADDLE VAT UNHAIRING EFFLUENT

Sieve No.	Sieve Opening (m.m.)	mg./l.							% Total Fat
		Total Solids	Screen* Solids	Suspended Solids	Volatile Suspended Solids	Total Nitrogen	Total Alkalinity ($CaCO_3$)	Chemical Oxygen Demand	
0		54,000		6,555	4,095	3,342	12,180	33,358	11.10
10	2.00	40,000	18,800	6,295	4,295	3,508	12,600	33,853	5.82
20	0.84	39,800	21,100	6,195	4,455	3,629	11,900	34,919	5.55
30	0.59	38,200	21,700	5,865	4,390	3,523	11,550	33,625	5.49
40	0.42	38,800	23,800	5,815	3,390	3,614	11,550	35,719	5.41
50	0.30	40,000	29,300	5,235	3,295	3,552	11,000	37,661	5.81

*Solids retained in screen.

$MnSO_4$ as a catalyst, has been demonstrated for several years. Bailey and Humphreys (9) and Eye and Clement (10) investigated this system for oxidation of sulfides in highly-alkaline lime-sulfide unhairing effluents. However, Cooper *et al.* (8) demonstrated that sulfides can be quantitatively eliminated from lime-sulfide unhairing effluents by bio-oxidation reactions with activated sludge from sanitary waste which has previously been acclimated to the unhairing effluents.

Effect of Screening. The effects of screening paddle vat effluent through different screen sizes are summarized in Table XII. The total solids decreased from 54,000 mg./l. to approximately 40,000 mg./l. through the 10 mesh screen, and remained nearly constant through the finer screens. The suspended solids decreased from about 6,500 mg./l. to 5,200 mg./l., and the volatile suspended solids decreased from 4,100 mg./l. to 3,300 mg./l. The solids retained on the screens increased from about 19,000 mg./l. to 29,000 mg./l. The total nitrogen in solution was approximately constant at about 3,500 mg./l., and the total fat, which was about 11 percent before screening, was nearly constatnt about 5.6 percent. The COD of the effluent increased slightly from 33,000 mg./l. to 37,000 mg./l. The most practicable screen size was the 20 mesh screen, since the effluent passed through this screen at a reasonably fast rate, whereas the finer mesh screens increasingly retarded the passage of effluent.

SUMMARY AND CONCLUSIONS

Effluent composition variables such as suspended solids content, salt concentration, age, dilution, pH, and previous treatment influence the efficiency of specific flocculation treatments for different lime-sulfide unhairing effluents. The flocculation and removal of suspended solids by specific polyelectrolytes was not affected by up to fourfold dilution of the effluents with water, and only moderately decreased by one to three weeks aging. Flocculant efficiency of the Primafloc flocculant system (PFA-10, PFC-3, and $(NaPO_3)_6$) on fresh hide paddle vat effluent was decreased slightly by the addition of up to five percent NaCl and moderately by eight percent NaCl. Aging combined with salt however, resulted in considerable losses of flocculant efficiency. Lowering the pH of the effluents from above 12 to 10 decreased the efficiency of the flocculant systems, and pH's of 8 or lower resulted in the liberation of H_2S and the precipitation of protein.

The selection of a flocculant system for a particular unhairing effluent must still be determined by trial on the effluent. The function of a flocculant system is to reduce the electrophoretic mobilities (zeta potentials) of the suspended solids to zero, and bring about coagulation. The information presented in this paper provides assurance that once the appropriate system is selected it can be used with a reasonable degree of confidence that the minor changes in dilution, age, pH, and salt concentration likely to be experienced in normal tannery operation will not produce major changes in flocculant efficiency.

We are optimistic that effective flocculating systems can be developed to remove suspended solids from unhairing effluents. This offers promise of service as an in-plant primary treatment of an unhairing effluent, either for a recycling process or for further treatment by bio-oxidation with acclimated activated sludge for removal of sulfide and for recovery of protein, or recovering the solids for use as ingredients of poultry or animal feeds or fertilizer mixes.

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DISCUSSION

Mr. Richard G. Waite (S. B. Foot Tanning Company): Thank you, Bill; that was a very interesting paper. We are all well acquainted with the problems related to the discharge of tannery wastes which have been heavily contaminated by the suspended matter generated during the beamhouse processes. Bill, could you give us an idea how effective your flocculating systems are in reducing the suspended solids in tannery effluents to meet the proposed EPA Guidelines?

Mr. Happich: According to the EPA Guidelines which were originally published in the Federal Register, April 9, 1974, by July 1, 1977, a proposed limit was 5 pounds of total suspended solids per 1,000 pounds of hide processed. For a tannery processing 350 hides per day and a total effluent volume of about a million gallons, this effluent would contain 90 p.p.m. of suspended solids if it meets the EPA Guidelines. Some of our figures were slightly higher than this, but we are approaching this level.

MR. WAITE: Thank you, Bill. Are there any questions from the floor?

DR. HARLAND YOUNG (Research Advisory Service): Your charts indicated that the effluent would be diluted at various levels up to three times. Did the concentration of the flocculant as added to the effluent remain constant?

MR. HAPPICH: Yes, I failed to mention that, but the flocculant was added at a constant amount, so that in effect the proportion of the flocculant to the solids was increasing.

DR. YOUNG: The second question which bears on the first: It has been found in many instances that recommended levels of the flocculant that is proportioned into the waste stream should not exceed 0.02 percent of the flocculant in the flocculant solution. We have found when that is violated by going up to high concentrations, you sometimes double and treble the amount of polymer used because of local overfloccing. But if that is diluted in line, so that when the more dilute polymer hits the stream, you can often get away with only one-third of the amount of polymer. The question is: Did you vary the concentration of the polymer solution as added? In other words, if you added 2 p.p.m. or 4 p.p.m. at one time, did you add 4 p.p.m. solution diluted to 0.005 percent solution or was it always at 0.1 or 0.2 percent, as the case was?

MR. HAPPICH: In our original experiments we varied the concentration up to as much as 100 p.p.m. in order to see in what range it was most effective.

DR. YOUNG: Maybe I haven't made myself clear. If you add a polymer solution proportionate to flow, that polymeric solution will be quite viscous. Sometimes it can be added 0.2 percent (meaning the concentration of the polymer solution and nothing to do with the ratio to the suspended solids); and then you can dilute it to 0.02 percent and add the same amount of polymer. My question is, did you always add the polymer solution; no matter how much you added, was it always at the same concentration?

MR. HAPPICH: Yes, it was. We usually added the polymer as a 0.1 percent solution to the effluent.

DR. YOUNG: Therefore, my suggestion would be that you consider diluting that polymer, maybe 10 or 20 to 1, and then use the same level. You may find that you will be able to get by with much less polymer on the total.

MR. HAPPICH: Thank you. We certainly will try it.

MR. WAITE: Are there any other questions?

Dr. Harlan (Eastern Regional Research Center, USDA): I want to point out, as Bill did in the paper, that we prediluted these polymer solutions to be sure that they were well dissolved and reasonably dispersed and then added aliquots of the prediluted polymer. I think it is an interesting experiment that we haven't reported on here. We did take steps to be sure that there was good dispersion and predilution of the polymers.

Mr. Wells (Bell, Galyardt and Wells): I came a little late to your paper and perhaps you have already answered the question. Did you tell who the manufacturers were of the flocculants that you used and how you arrived at the primafloc formula?

Mr. Happich: Primaflocs are products of Rohm and Haas Company, Philadelphia, Pa., and X-400 is made by Estech Inc., Chicago, Ill.

Mr. Waite: Perhaps, Bill, you would like to comment on what the cost of these polymers would be in relation to reduction of suspended solids.

Mr. Happich: From the concentrations that we presented, the cost of treating 10,000 gallons of undiluted effluent from the unhairing operation would probably vary from 40 cents to a dollar for the chemicals alone.

Mr. Waite: If there are no more questions, I want to thank you again, Bill, for a very fine paper.